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Small-Angle X-Ray Scattering Studies on Spontaneous Perpendicular Orientation of Cylindrical Microdomains in a Block Copolymer Film

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Block copolymers undergo microphase separation in several tens of nanometers, because of strong segregation between constituent block chains comprising different chemical species. Depending on composition, the morphology of the microphase-separated structures can be altered from spheres, cylinders, or gyroid to lamellae. It is well known that physical properties of block copolymers strongly depend on the morphology. Not only the morphology, but the orientation of microdomains are key factors to be taken into account in order to control materials properties more efficiently, such as imparting anisotropy of properties. To control orientation of microdomains is therefore one of the fundamental ways to novel specialty materilas. Generally, imposing a flow field works well to orient cylindrical microdomains such that the cylinders orient parallel to the flow.

To our best knowledge, there is no report of perpendicular orientation of cylinders in a thick film (thickness in 0.1 ~ 1.0 mm range). Self-organization ability of block copolymer may be applied to this problem. One of the promising strategies is a directional coalescence of spherical microdomains in the direction perpendicular to the sample film, as shown in Figure 1. In this concept, the resultant cylinders are spontaneously oriented perpendicularly.

The sample used is an triblock copolymer (M_n = 6.6×10^4, M_w/M_n = 1.03, volume fraction of PS is 0.16, volume fraction of butylene moiety in PEB block chain is 0.41. PS: polystyrene, PEB: polyethylenebutylene). A selective solvent n-heptane was used for the solution casting, where n-heptane is good for PEB and poor for PS. The thickness of the as-cast film was approximately 0.5 mm. The as-cast film was subjected to heating at 2°C/min from 70.0 to 237.7°C in a silicone-oil bath. In this process, two-dimensional small-angle X-ray scattering (2d-SAXS) time-resolved measurements were performed.

Figure 2 shows the edge view 2d-SAXS patterns for the SEBS sample cast from the n-heptane solution at various temperatures in the range from 70.0 to 237.7°C. For 70.0 ~ 90.0°C, the 2d-SAXS pattern was elliptic. When the sample heated up higher than the glass transition temperature of PS (100°C), the pattern transformed into a round shape, which actually took place around 120 ~ 130°C. It was found, however, that the spherical morphology still remained, i.e., spheres did not transform into cylinders yet. The transition took place much more later as the temperature proceeded to the range of 215 ~ 230°C. Right after the transition, it was found that the resultant cylinders already oriented perpendicularly, as shown in Figure 2. Although at 233.6°C the orientation reached the best, it was suddenly randomized. It is because the sample underwent transition to the disordered micelle state and therefore the cylindrical microdomains disappeared.

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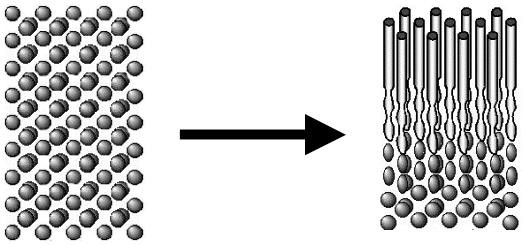

Figure 1. Schematic representation of a directional coalescence of spherical microdomains.

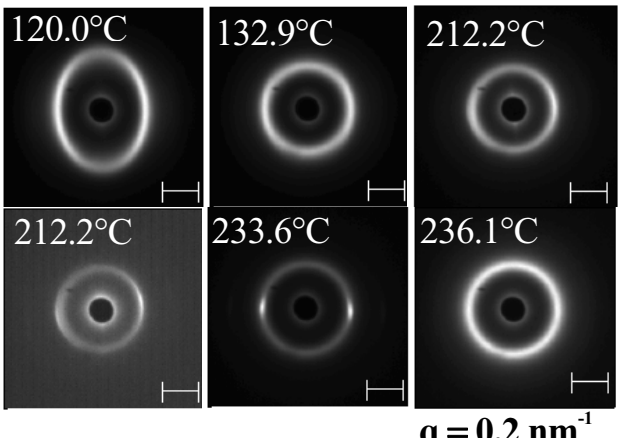

Figure 2. Edge view 2d-SAXS patterns at various temperatures in the range of 70.0°C to 236.1°C